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Emergency sorbents for oil and petroleum product spills based on vegetable raw materials

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Abstract. Protection against the oil and petroleum product spills in case of accidents is an important environmental issue.The possibility of liquidation of crude oil and oil product spills from a solid surface has been established, using the waste of the agricultural complex (husks of barley, pericarp radish, pericarp (shell) of peanuts). The sorption ability of agricultural complex waste in relation to crude oil and oil products with various density has been studied. A comparative analysis of the proposed oil and petroleum product removal during emergency spills demonstrated its high efficiency due to the low cost and wide resource base, sufficient petro conductivity, the possibility of using hydrocarbon saturated sorbents without re-contaminating the environment.

1. Introduction

The rate of accumulation of petroleum products as a result of anthropogenic pollution in water and soil ecosystems is far ahead of their rate of biodegradation in a natural way, and existing technologies do not allow to cope with such contamination quickly and efficiently. Sorbent materials can provide a useful resource in a response to a spill of oil, allowing oil to be recovered in situations that are unsuitable for other techniques [1,2]. The hit of oil and its products into the environment, either in air, water or soil, causes a change in their physical, chemical and biological characteristics, disrupting the natural course of biochemical processes. Elimination of oil pollution is not without the use of various types of sorption materials. Oil sorbents are materials that can absorb oil products in large quantities, however preventing their migration in the surrounding environment [3-19].

A special interest is the research and study of materials that have high sorption characteristics and have an organic basis. This fact is very important, since by solving problems of recycling and (or) regeneration of sorbents, in the case of their organic basis, their rational use, for example, for obtaining thermal energy, without secondary pollution of the environment, is possible. In recent years, a search has been actively carried out in the field of obtaining non-expensive oil sorbents for the collection of hydrocarbon spills:

- Usage of untreated plant residual. For example, a method for producing an oil sorbent based on untreated husks (hulls) grains of buckwheat by repeatedly applying it to an oil stain on the surface of water with subsequent collection, for example, using a grid [3].
- Thermal methods for production oil sorbents from based on vegetables raw materials of agroindustrial complex, for example, carbonized husk of buckwheat grains, carbonized

residual of barley production, carbonated rice husks, carbonized husk of rice grains, the product of pyrolysis of rice husks, carbonized sunflower husks, modified and carbonized sunflower husks. A common deficiency of thermal methods for production oil sorbents is the need for high-temperature treatment of plant resources of the agroindustrial complex for the purpose of transferring them to ash or activated carbon. Usage of these methods reduces the outlet of the sorbent due to pyrolysis and carbonization of the secondary plant resources of the agroindustrial complex and leads to the loss of a significant part of the organic component of the residual that can be a source for producing a number of valuable organic substances (polysaccharides, pigments, etc.); Moreover, these methods require high energy costs and the use of energy-intensive expensive equipment, often difficult to operate [3].

- Methods for producing oil sorbents from plant resources of the agroindustrial complex, based on chemical modification of raw materials, for example, producing sorbents from walnut shells treated with concentrated hydrochloric acid and then with 33% sodium hydroxide solution to remove ballast substances; from the residual of processing of grain and oilseeds by treating them with carbon dioxide in supercritical conditions at a temperature of 40-60 °C and a pressure of 10-25 MPa; on the basis of buckwheat husk, treated in an extractive solution of ammonium oxalate or mineral acid (hydrochloric, sulfuric or nitric acids) at a concentration of 0.1-0.5 at 60-90 °C; from rapeseed or rape cakeoil, which is exposed to hydrolysis with 30-50% acid solution, sorption was carried out by metal ions. General defect of these methods is the need to use concentrated acids and bases, chemically resistant equipment, supercritical conditions, multi-step processes, and formation of toxic sewage [3].

2. Purpose and objectives of the study

Despite the development in this direction, the issues of research of the collection of oil and oil products from various surfaces and the estimate effectiveness of the usage of sorbents on the basis of the agroindustrial complex's residual are not given enough attention, which determined the purpose of this research. For the research, the following residual samples of agroindustrial complex are considered: Buckwheat husk Fagopyrum esculentum, Buckwheat husk Fagopyrum esculentum, Peanut pericarp Arachis hypogaea and Pericarp of radis Raphanus.

3. Research methods

The initial samples were dried up to a moisture content of not more than 10% by weight. and several steps of crushing: the first step of grinding on a disk hipper machine, in the second step, the particles of the crust were regrinded to obtain 1.0 mm grain-size, by dry mechanical grinding. After grinding, the samples were exposed to dry fractionation on laboratory sieves, a fraction of 0.25-1 mm was isolated for investigation. Then, the samples were processed in three ways:

1) 1 kg of raw material was loaded into an extractor with a stirrer, which was fed distilled water, the mass ratio of raw materials: water (1:50) - (1:100). Process conditions: temperature (23 ± 2)° C and atmospheric pressure. Extraction time - 48 hours, the mixing constant. The solid residue was filtered on a porous filter and dried at a temperature (103 ± 2)°C to constant weight. The sorbent outlet was 82.5% by weight of the barley husk, 92.3% by weight. % of radish pericarp and 95.0% of peanut pericarp.

2) 1 kg of raw material was loaded into an extractor with a stirrer, a jacket (electric heating) and refrigerator-condenser, which was fed distilled water, the mass ratio of raw material: water (1:50) - (1: 100). Process conditions: temperature (100 ± 5)°C and atmospheric pressure. The extraction time is 3 hours; the mixing is constant. The solid residue was filtered on a porous filter and dried at a temperature (103 ± 2) °C to constant weight mass. The sorbent outlet was 81.1% by weight. of husks (husks) of barley, 91.2% by weight. % of radish pericarp and 85.5% of peanut pericarp.

3) 1 kg of raw material was loaded into an extractor with a stirrer, a jacket (electric heating) and refrigerator-condenser, which was fed 1 - 1.5% aqueous solution of sodium hydroxide, the mass ratio of raw materials: dissolving sodium hydroxide (1:50) - (1:100). Process conditions: temperature (101

± 2)°C and atmospheric pressure. The extraction time is 1 hour, the mixing is constant. The solid residue was filtered on a porous filter, rinsed with distilled water until neutral and dried at a temperature (103 ± 2)°C to constant weight. The outlet of sorbent is 39.5% by weight. of the husks (husks) of barley, 45% of the weight. % of radish pericarp and 56.6% of peanut pericarp.

By evaluating the effectiveness of the oil sorbent, they should be guided to the main criteria: their capacity relative to oil, degree of hydrophobicity, buoyancy after oil sorption, the possibility of oil desorption, regeneration or utilization of the sorbent.

Addition of hydrophobic surface can eliminate the high absorption of water. With low buoyancy of sorbing materials, they can be used in products with reinforcing sheaths - mats or booms.

For the obtained products, the adsorption capacity is determined according to iodineand methylene blue methods [3]. The analysis was performed on an Atomic Force Microscopy (AFM). The sorption capacity (oil capacity) with respect to oil and oil products (kerosene, diesel fuel and first vacuum distillate) is determined by the known method [20]. The water-repellency treatment (hydrophobization) of the surface is carried out in various ways [4].

4. Results and discussion

The biggest outlet of the sorbent from the three proposed methods, obtained by the first method, cold water extracted mainly ballast extractives such as monosaccharides, dyes, glycosides, a lower flowrate of oil sorbent obtained with hot extraction by water in the second way, as long as besides monosaccharides, glycosides, proteins, amino acids, pectic substances and mono-oligo- and polysaccharides are also removed. The outlet of the oil sorbent is 40-57% by weight. from the considered residual of the agroindustrial complex used in the third method, where the extracted materials were diluted with aqueous sodium hydroxide solution: resins, fats, polyphenolic acids, lignin humic substances, low molecular weight lignin, polysaccharides.

Adsorption activity on iodine characterizes the volume of micropores (about 1 nm) and, respectively, the ability to adsorb relatively low molecular organic substances [3]. It can be seen from Table 1 that according to this indicator, the samples obtained are close to industrial enterosorbents, for example, Belarusian enteric sorbent "Polifam" (adsorption activity for iodine is 24.16%) and to the Russian brand "Polyphepan" (29.63%), which indicates the development of the porous structure of the residues using the proposed methods 1-3.

Table 1. Presents generalized data of the adsorption capacity.

Name of sorbent	Adsorption capacity			
	In natural form	According to 1st method after cold extraction	According to 2nd method after hot extraction	According to 3rd method after base treatment
Adsorption capacity by iodine, %				
Pericarp of radish	24,36	24,78	26,88	28,98
Barley husks	22,37	22,47	23,52	28,56
Peanut pericarp	17,15	19,47	21,00	24,56
Buckwheat husk	15,33	17,64	21,84	24,36
Adsorption capacity for methylene blue, mg /g				
Pericarp of radish	146,23	195,23	195,61	225,10
Barley husks	95,11	143,33	180,00	210,00
Peanut pericarp	62,50	71,25	159,17	174,17
Buckwheat husk	15,16	35,31	60,27	78,92

Adsorption capacity on methylene blue allows to evaluate the content of micropores in the sorbent with effective diameters of 1.5-1.7 nm and indirectly characterizes the sorption ability in relation to oil products [3,4].

Table 1 shows that the treatment of samples with distilled water and dissolved base, leads to form additional pores up to 1.7 nm. It should be considered that, according to this indicator, the sorbents obtained by the third method from radicates of radish and barley husks are more effective than the commercially produced enterosorbents activated carbon (210 mg /g) and Polyphepan (125.8 mg / g).

The microstructure of the samples is analyzed on an atomic force microscope Figure 1. In the obtained images the width and depth of the pores were measured. The analysis showed that the porosity of the surface of the Barley husk (Figure 1, b) is more developed than that of Buckwheat husks (Figure 1, a).

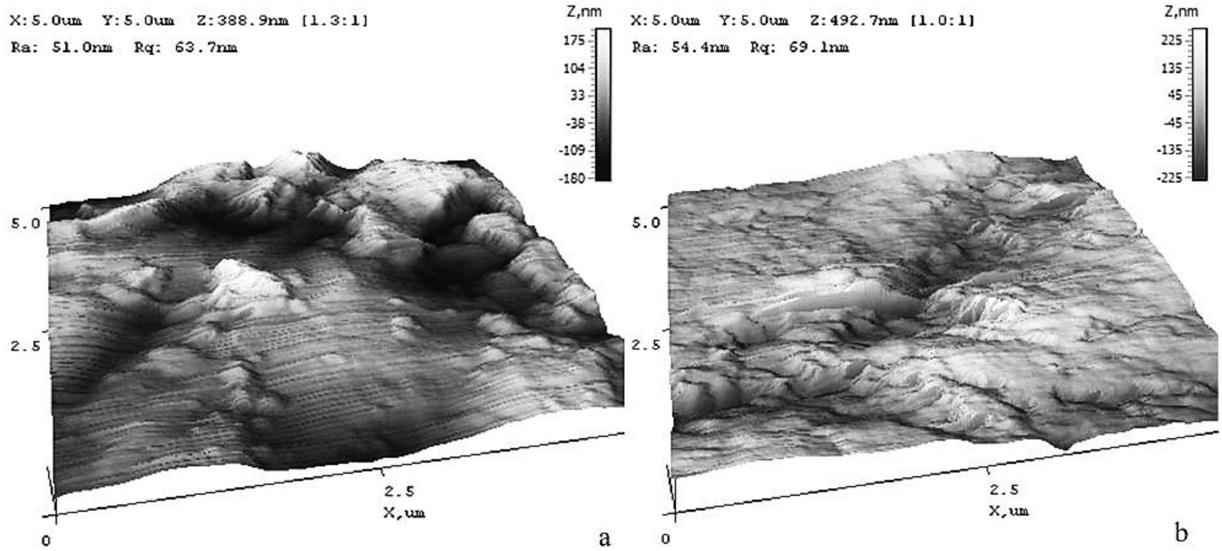

Figure 1. Analysis performed on an AFM (a-surface Buckwheat husk, b -surface Barley husk).

The sorption capacity (oil capacity) with respect to oil and petroleum products (kerosene, diesel fuel and first vacuum distillate, produced by JSC "Naftan") is presented in Table 2. Analysis of the sorption capacity of agricultural residual with respect to oil and petroleum products showed that when they are treated with cold water by the first method due to an increase in the volume of pores in solid residues, the sorption capacity increases by 1.9 times for oil of peanut pericarp, 3 times for the husks of barley, 3.7 times for the pericarp radishes. Treating with hot water leads to an increase in pore volume of solid residues, the sorption capacity increases by 2.3 times for oil for peanut pericarp, 3.2 times for barley husks, 4.0 times for pericarp radishes. Treating with weak sodium hydroxide solution leads to an increase in pore volume in solid residues leads to an increase in sorption capacity by oil 2.5 times for peanut pericarp, 4.2 times for barley husks, 5.5 times for radish pericarp. However, the sorption capacity of sorbents of more than 3.0 g / g is economically effective with treatment by all three methods.

To eliminate the high absorption of water of the samples, studies were performed on the water-repellency treatment [4] of the surface of the barley husk with vapors of heavy pyrolysis resin, polymethylmethyl siloxane (of various concentrations) and treatment with 2% by weight HCl to extract. As a result, the best performance is obtained by extracting with 2% by weight HCl, which allowed to significantly reduce the water absorption of samples, increase buoyancy and oil capacity (the result is presented in the table 3).

Due to environmental compatibility, wide raw material base, relatively high oil capacity and at a low cost (for example, the price of sorbents based on barley husk can be up to 130 $ /t), sorbents based on agroindustrial residuals can successfully compete with industry produced by analogues (for example, widely used in Republic of Belarus for collection during oil and oil product spills in the oil refining plants, in transport, railway and airlines, and at the petrol stations, sorbent from the milled peat "Belneftesorb - extra" (at a price of about 400 $ /t), the sorption capacity for crude oil of which, as indicated by the producer, is up to 3 kg of pollutant per 1 kg of sorbent).

Table 2. Sorption capacity with respect to oil and petroleum products.

Name of sorbent	Oil capacity (sorption capacity), g/g			
	In natural form	According to 1st method after cold extraction	According to 2nd method after hot extraction	According to 3 rd method after base treatment
Sorption ability with respect to oil (density 861 g / cm³)				
Pericarp of radish	2,42	9,00	9,76	13,25
Barley husks	3,07	9,26	9,96	12,80
Peanut pericarp	2,29	4,55	5,32	5,74
Buckwheat husk	1,12	1,25	1,53	2,65
Sorption ability with respect to the first vacuum (oil) distillate (density 886 g / cm³)				
Pericarp of radish	2,71	7,89	7,93	15,45
Barley husks	3,16	7,42	7,68	15,25
Peanut pericarp	2,80	3,53	3,86	4,72
Buckwheat husk	1,14	1,62	1,64	1,96
The sorption capacity with respect to diesel fuel (density 825 g / cm)				
Pericarp of radish	2,43	7,11	7,65	13,18
Barley husks	3,00	8,64	7,88	9,68
Peanut pericarp	2,32	4,75	4,99	4,97
Buckwheat husk	0,96	1,03	2,08	2,05
Sorption ability with respect to kerosene (density 787 g / cm³)				
Pericarp of radish	2,35	7,01	7,53	11,93
Barley husks	3,06	7,09	7,55	10,43
Peanut pericarp	2,34	3,06	3,74	3,86
Buckwheat husk	0,89	1,37	1,69	2,42

Table 3. Water-repellency treatment of surface.

Processing method	Buoyancy, %	Water absorption, g /g	Oil capacity, g / g
Barley husks in untreated form	30	5,41	3,07
Barley husks treated with 100 % by weight of heavy pyrolysis resin	48	4,20	4,47
Barley husks treated with 2 % by weight aqueous solution of HCl	64	3,49	7,64
Barley husks treated with aqueous solution of polymethylsiloxane liquid			
1 % by weight	46	5,87	5,83
5 % by weight	46	3,80	5,71
100 % by weight	65	3,06	5,12

5. Conclusion

Thus, a sorbent with a high sorption capacity for collecting oil and petroleum products during their spills by disposing residual from the agroindustrial complex: barley husks, radish radishes and peanuts was obtained in a low-cost way. During the tests set their absorption efficiency of oil and petroleum products, as well as the use of economic rationality. These sorbents are not inferior in oil sorption known industrial sorbents. The offered sorbents can be dissipated during cleaning of various polluted surfaces of water, concrete, asphalt, metals, soil (clay, sand) from the pollutant by hand, by mechanical or pneumatic devices, further assembled conglomerate of hydrocarbon impregnated sorbent can be subjected to extraction of oil (oil product) by compression methods. The residue can be used as fuel briquettes with an increased calorific value. Petroleum sorbents from agroindustrial residual have the ability to biodegrade under the influence of aboriginal soil or artificially introduced microorganisms. It should be noted that it is advisable to obtain data sorbents in environmental and economic terms, due to the low cost of materials, easy manufacturing, high sorption properties, the possibility of recycling of secondary raw materials.

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